Supporting information

For

Highly active zinc alkyl cations for the controlled and immortal ring-opening polymerization of ε-caprolactone

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General procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a MBraun Unilab glovebox. THF, dichloromethane, and pentane were first dried through a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4Å) in a glovebox prior to use. CD_2Cl_2 and C_6D_6 were purchased from Eurisotope (CEA, Saclay, France), degassed under a N_2 flow, and stored over activated molecular sieves (4Å) in a glovebox prior to use. ε-caprolactone was purchased from SIGMA-ALDRICH, distilled over CaH_2 and subsequently stored on activated molecular sieves (4Å). All other chemicals were used as received. Ligands BIAN-Ar (Ar = Mesityl or Ar = 2,6-^{i}Pr$_2$Ph) were synthesized according to well-established literature procedures. NMR spectra were recorded on Bruker AC 300, 400 or 500 MHz NMR spectrometers in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H, ^{13}C and ^{19}F chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks, ^{11}B chemical shifts are given with $BF_3{\cdot}OEt_2$ as reference. IR spectra were recorded in the region 4000-100 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. Maldi-TOF analyses were carried out by the "Service de spectrométrie de masse de l'Université de Strasbourg" on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany), using dithranol (1.8.9 trihydroxyanthracene) as a matrix.

Synthesis of the neutral Zn complex (BIAN-Mes)ZnMe$_2$ (2a).

One equivalent of a precooled solution (-35 °C) of $ZnMe_2$ (240 μL, 2 M in toluene) was added to a toluene suspension (also cooled -35 °C) of the BIAN-Mes ligand **1a** (0.48 mmol, 200.0 mg). The reaction mixture was then allowed to warm up to room temperature under stirring during 2 hours. The resulting red solid was then filtered through frit, washed twice with pentane and dried *in vacuo (*0.210 g, 85 % yield). NMR analysis showed the latter solid to be NMR-pure species **2a**, which was subsequently used as it. Anal. Calc. for $C_{32}H_{34}N_2Zn$ (512.01): C, 75.07; H, 6.69; N, 5.47. Found: C, 74.80; H, 6.59; N, 5.56. FTIR: ν_{max}(solid)/cm^{-1}: 1674s (C=N), 1647s (C=N). ^{1}H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.02 (d, ^3J = 8.4 Hz, 2H, Ar), 7.48 (dd, ^3J = 8.4, 7.3 Hz, 2H, Ar), 7.06 (s, 4H, Ar), 6.82 (d, ^3J = 7.3 Hz, 2H, Ar), 2.41 (s, 6H, C*H*$_3$ *para*-Mes), 2.16 (d, 12H, C*H*$_3$ *ortho*-Mes), -0.85 (s, 6H, Zn-

CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) = 162.4, 143.6, 142.9 135.6, 131.4, 130.6, 131.4, 129.8, 129.4, 128.9, 128.6, 128.5, 127.3, 125.6, 123.9, 21.0, 18.2, -8.2.

Synthesis of the salt species [3a - 3b][MeB(C_6F_5)$_3$].

First method: One pot procedure

One equivalent of a precooled solution (-35 °C) of $ZnMe_2$ (240 μL, 2 M) in toluene was added to a toluene suspension (also cooled -35 °C) of the BIAN-Mes **1a** or **1b** (0.48 mmol, 200.0 mg for **1a** and 240.0 mg for **1b**). The reaction mixture was allowed to warm up to room temperature and stirred for one hour. The reaction mixture was then cooled again to -35 °C and the sequential addition of two equivalents of THF (0.96 mmol, 80.0 mg) and then one equivalent of $B(C_6F_5)_3$ (0.48 mmol, 245.0 mg) was carried out. The reaction was left under stirring for additional 2 hours. The solvent was evaporated under vacuum to quantitatively afford the corresponding salt species [(BIAN-Ar)Zn(Me)(THF)][$MeB(C_6F_5)_3$] ([**3a-b**][$MeB(C_6F_5)_3$], 310 mg and 69 % yield, 410 mg and 72 % yield, respectively) as deduced from NMR data.

*Second method: from species **2a** to access* [**3a**][$MeB(C_6F_5)_3$]

To a suspension of compound **2a** (0.39 mmol, 200.0 mg) in toluene at -35 ºC, the sequential addition of two equivalents of THF (0.78 mmol, 64 mg) and then one equivalent of $B(C_6F_5)_3$ (0.39 mmol, 200.0 mg) was carried out. The initial red suspension quickly turned into a red bright color solution and it was allowed to warm up to room temperature under stirring. After 2 hours the solvent was removed under vacuum. The resulting red/orange product was washed with pentane to quantitatively afford the salt species [(BIAN-Mes)Zn(Me)(THF)][$MeB(C_6F_5)_3$] ([**3a**][$MeB(C_6F_5)_3$], 310.0 mg, 84% yield), as deduced from NMR data.

Characterization data for [(BIAN-Mes)Zn(Me)(THF)][MeB(C_6F_5)$_3$] ([**3a**][$MeB(C_6F_5)_3$]).

Anal. Calc. for $C_{54}H_{41}BF_{15}N_2OZn$ (1095.08): C, 59.23; H, 3.77; N, 2.56. Found: C, 59.05; H, 3.73; N, 2.50. FTIR: ν_{max}(solid)/cm^{-1}: 1628s (C=N), 1603s (C=N). ^1H NMR (300 MHz, CD_2Cl_2): δ (ppm) = 8.23 (d, ^3J = 8.4 Hz, 2H, Ar), 7.65 (dd, ^3J = 8.4 and 7.3 Hz, 2H, Ar), 7.16 (s, 4H, Ar), 7.01 (d, ^3J = 7.3 Hz, 2H, Ar), 3.80 (br, 4H, CH_{2THF}), 2.43 (s, 6H, CH_3 *para*-Mes), 1.30 (d, 12H, CH_3 *ortho*-Mes), 1.92 (br, 4H, CH_{2THF}), 0.43 (s, 3H, CH_3-BAr^F), -0.49 (s, 3H, Zn-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) = 166.7, 146.9, 139.9, 138.7, 133.8,

131.4, 130.8, 129.9, 128.5, 128.2, 126.6, 125.6, 125.4, 71.1, 25.6, 21.1, 18.1, -13.7. $^{19}F\{^{1}H\}$ NMR (282 MHz, CD_2Cl_2): δ (ppm) = -133.2 (d), -165.4 (t), -168.0 (t). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2): δ (ppm) = -15.2.

NMR data for [(BIAN-Dipp)Zn(Me)(THF)][MeB(C_6F_5)$_3$] ([**3b**][MeB(C_6F_5)$_3$]).

Anal. Calc. for $C_{60}H_{53}BF_{15}N_2OZn$ (1179.24): C, 61.11; H, 4.53; N, 2.38. Found: C, 61.03; H, 4.54; N, 2.30. FTIR: ν_{max}(solid)/cm^{-1}: 1621s (C=N), 1587s (C=N). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.24 (d, ^{3}J = 8.4 Hz, 2H, Ar), 7.65-7.56 (m, 4H, Ar), 7.47-7.46 (m, 4H, Ar), 6.81 (d, ^{3}J = 7.3 Hz, 2H, Ar), 3.85 (br, 4H, CH_{2THF}), 2.89 (spt, ^{3}J = 6.8 Hz, 4H, CH(CH_3)$_2$), 1.95 (br, 4H, CH_{2THF}), 1.30 (d, ^{3}J = 6.8 Hz, 12H, CH(CH_3)$_2$), 0.94 (d, ^{3}J = 6.8 Hz, 12H, CH(CH_3)$_2$), 0.44 (s br, 3H, CH_3-BAr^F), -0.42 (s, 3H, Zn-CH_3). $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2): δ (ppm) = 167.9, 140.0, 139.3, 137.8, 134.5, 131.64, 129.8, 128.6, 127.9, 125.9, 70.9, 29.9, 25.8, 24.4, 24.3, 1.2, -14.75. ^{19}F NMR (282 MHz, CD_2Cl_2): δ (ppm) = -133.2 (d), -165.5 (t), -168.0 (t). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2): δ (ppm) = -15.1.

Synthesis of the neutral Zn-Et complex [(^{Et}BIAN-Mes)Zn(Et)] (4a).

One equivalent of a precooled solution (-35 °C) of $ZnEt_2$ (480 µL, 1M in toluene) was added to a toluene suspension (also cooled -35 °C) of the BIAN-Mes ligand **1a** (0.48 mmol, 200.0 mg). The reaction mixture was allowed to warm up to room temperature under stirring during 2 hours. The solvent was evaporated under vacuum and the obtained solid washed twice with pentane to yield NMR-pure complex **4a (**brown solid, 0.21 g, 81 % yield), whose proposed formulation was confirmed by X-ray crystallography. Suitable crystals for X-Ray analysis were obtained by slow vapour diffusion of pentane into a toluene solution of **4a**. Anal. Calc. for $C_{34}H_{38}N_2Zn$ (540.06): C, 75.61; H, 7.09; N, 5.19. Found: C, 75.70; H, 7.03; N, 5.26. FTIR: ν_{max}(solid)/cm^{-1}: 1650vs (C=N). ^{1}H NMR at 267 K (500 MHz, CD_2Cl_2): δ (ppm) = 7.93 (d, ^{3}J = 8.2 Hz, 1H, Ar), 7.68 (d, ^{3}J = 8.2 Hz, 1H, Ar), 7.35 (dd, ^{3}J = 8.4 Hz, 7.2 Hz, 1H, Ar), 7.32 (dd, ^{3}J = 8.4 Hz, 7.2 Hz, 1H, Ar), 7.08 (br s, 1H, CH-Mes), 7.00 (br s, 1H, CH-Mes), 6.98 (br s, 1H, CH-Mes), 6.66 (br s, 1H, CH-Mes), 6.65 (d, ^{3}J = 7.2 Hz, 1H, Ar), 2.62 (s, 3H, CH_3-Mes), 2.39 (s, 3H, CH_3-Mes), 2.33 (dq, $^{2}J_{HaHb}$ = 13.2 Hz, ^{3}J = 7.3 Hz, 1H, C_{quat}-CH_aH$_b$-CH_3), 2.29 (s, 3H, CH_3-Mes), 2.26 (s, 3H, CH_3-Mes), 2.13 (dq, $^{2}J_{HaHb}$ = 13.2 Hz, ^{3}J = 7.3 Hz, 1H, C_{quat}-CH$_a$$H_b$-$CH_3$), 2.03 (s, 3H, CH_3-Mes), 1.32 (s, 3H, CH_3-Mes), 1.00 (dd, ^{3}J = 8.0 Hz, 8.0 Hz, 3H, Zn-CH_2-CH_3), 0.48 (dd, ^{3}J = 7.3 Hz, 7.3 Hz, 3H, C_{quat}-CH_2-CH_3), 0.33-0.20 (m, 2H, Zn-CH_2-CH_3). $^{13}C\{^{1}H\}$ NMR at 267 K (CD_2Cl_2 125 MHz): δ (ppm) = 191.0

(C_{quat}, N=C), 143.8 (C_{quat}, Ar), 143.2 (C_{quat}, Ar), 149.4 (C_{quat}, Ar), 140.2 (C_{quat}, Ar), 140.1 (C_{quat}, Ar), 136.9 (C_{quat}, Ar), 135.1 (C_{quat}, Ar), 131.3 (C_{quat}, Ar), 131.1 (C_{quat}, Ar), 131.0 (CH, Ar), 130.1 (CH, Mes), 129.9 (C_{quat}, Ar), 129.8 (CH, Mes), 129.1 (CH, Mes), 128.8 (CH, Mes), 128.6 (C_{quat}, Ar), 128.5 (CH, Ar), 128.0 (CH, Ar), 127.1 (C_{quat}, Ar), 123.6 (CH, Ar), 123.2 (CH, Ar), 121.5 (CH, Ar), 79.1 (C_{quat}, *C_{quat}*-Et), 44.8 (CH_2, C_{quat}-*Et*), 21.1 (CH_3, Mes), 21.0 (CH_3, Mes), 20.9 (CH_3, Mes), 20.8 (CH_3, Mes), 18.9 (CH_3, Mes), 18.4 (CH_3, Mes), 11.7 (CH3, C_{quat}-*Et*), 10.3 (CH_3, Zn-*Et*), 0.4 (CH_2, Zn-*Et*).

General procedure for ε-caprolactone polymerization

Solution polymerization conditions

In a glovebox, the desired Zn initiator was charged in a vial equipped with a TeflonTM-tight screw-cap and a monomer (M) solution ($[M]_0$ = 1M, THF as a solvent) containing the appropriate quantity of alcohol (BnOH or (-)-menthol) was added *via* a syringe all at once. The solution was heating at 60 °C under vigorous stirring for the appropriate time. Aliquots were taken and analysed by ^{1}H NMR spectroscopy to estimate the conversion as the ROP reaction proceeded. The reaction mixture was quenched with cold MeOH provoking the precipitation of the polymer, which was then washed several times with MeOH, dried in *vacuo* until constant weight and subsequently analyzed by ^{1}H NMR and SEC. In some cases, a MALDI-TOF-MS analysis was performed.

Bulk polymerization conditions

In a glovebox, the desired initiator Zn initiator and the appropriate quantities of monomer and alcohol (BnOH or (-)-menthol) were charged in a small vial equipped with a Teflon-tight screw-cap. The solution were heated at 60°C and kept at this temperature for the desired time. An identical work-up to that described above was performed.

Size-exclusion chromatography (SEC)

The number-average, weight-average molar masses (Mn and Mw, respectively) and molar mass distribution (Mw/Mn) of the polycaprolactone (PCL) samples were determined by size exclusion chromatography (SEC) at 40°C with Shimadzu LC20AD ultra-fast liquid chromatography equipped with a Shimadzu RID10A refractometer detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. A Varian PLGel pre-column and a Varian PLGel 5 μm were used. Calibrations were performed using polystyrene standards (400-100 000 g/mol) and raw values of M_n (SEC) were thus obtained. These values were corrected using the correction factors 0.56 as reported in the literature [$\boldsymbol{M}_{\mathbf{n(correc.)}} = 0.56 \,.\, \boldsymbol{M}_{\mathbf{n(SEC)}}$].[1]

[1] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* **2002**, *203*, 889.

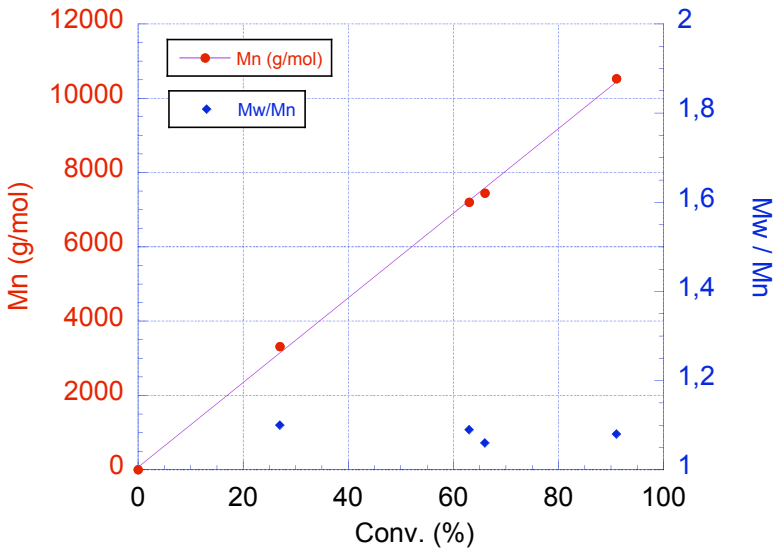

Figure S1: *Dependence of M_n (•) and polydispersity index M_w/M_n (⬩) of ε-PCL on monomer conversion for ε-CL polymerization using initiator **[3a]**[$MeB(C_6F_5)_3$] in THF at 60 °C in the presence of BnOH, **[3a]**[$MeB(C_6F_5)_3$]/BnOH/M_0 = 1/3/300 (M_n and PDI determined by SEC).*

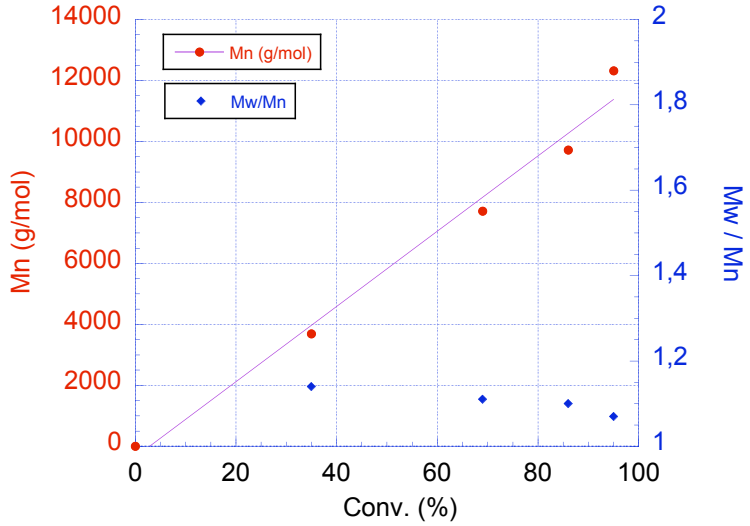

Figure S2: *Dependence of M_n (•) and polydispersity index M_w/M_n (⬩) of ε-PCL on monomer conversion for ε-CL polymerization using **[3b]**[$MeB(C_6F_5)_3$] in THF at 60 °C in the presence of BnOH, **[3b]**[$MeB(C_6F_5)_3$]/BnOH/M_0 = 1/3/300 (M_n and PDI determined by SEC).*

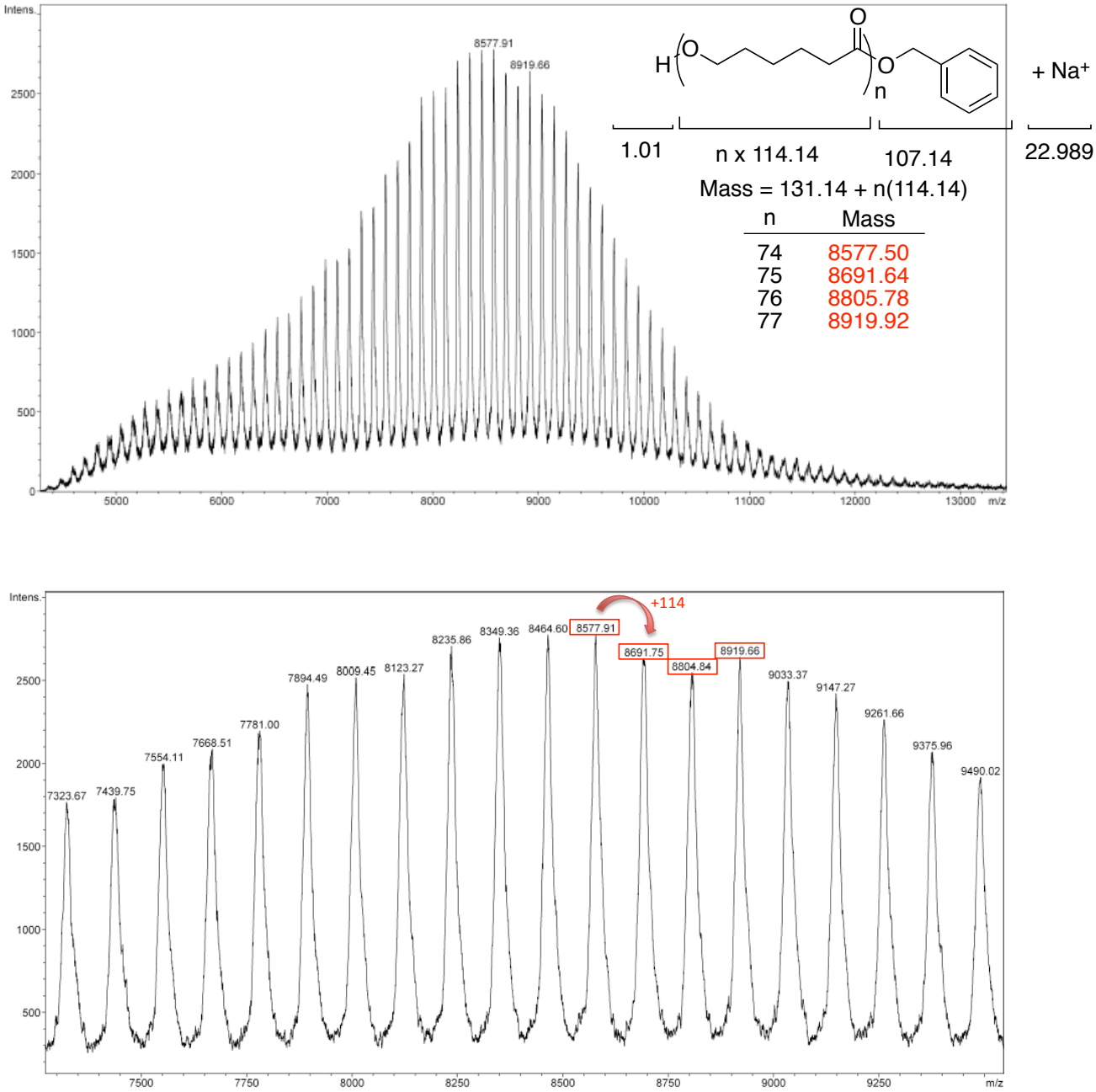

Figure S3-S4: MALDI-TOF mass spectra (full view and zoom) of linear ε-PCL prepared via the ROP of ε-caprolactone initiated by complex [**3b**][$MeB(C_6F_5)_3$]. Reaction conditions: ([**3b**][$MeB(C_6F_5)_3$]/BnOH/M_0) = (1/3/300), THF, 95% conversion).

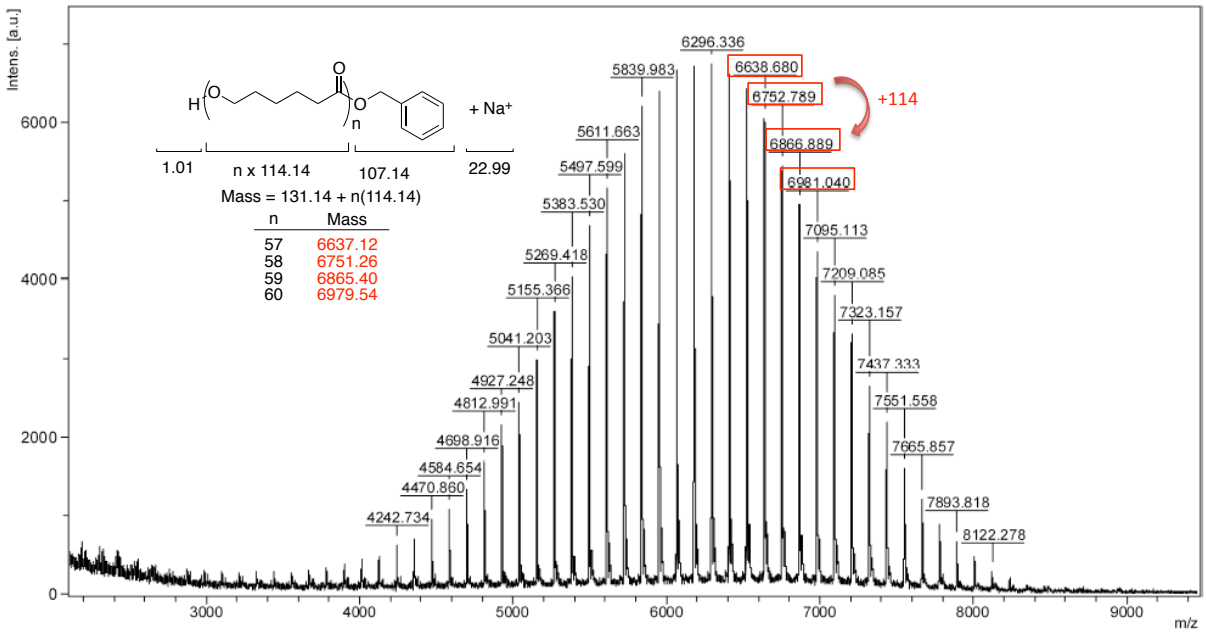

Figure S5: MALDI-TOF mass spectrum of linear ε-PCL prepared via the ROP of ε-caprolactone initiated by complex [**3a**][$MeB(C_6F_5)_3$]. Reaction conditions: ([**3a**][$MeB(C_6F_5)_3$]/BnOH/M_0) = 1/3/300, THF, 63% conversion.

==== Shimadzu LCsolution GPC Analysis Report ====

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Sample ID	:
Vail#	:
Injection Volume	: 100 uL
Data Filename	: CRV-63-PCL.lcd
Method Filename	: Etalon PS30.lcm
Batch Filename	:
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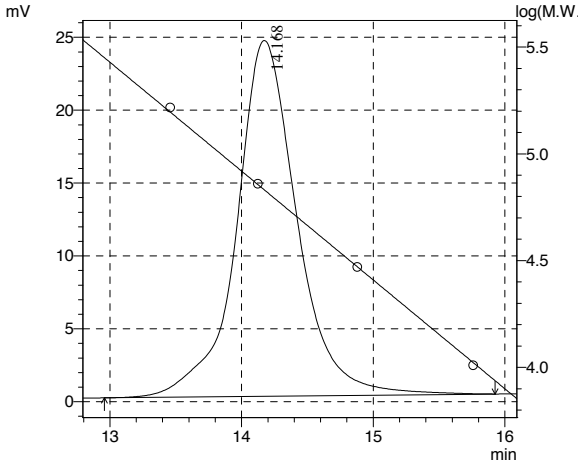
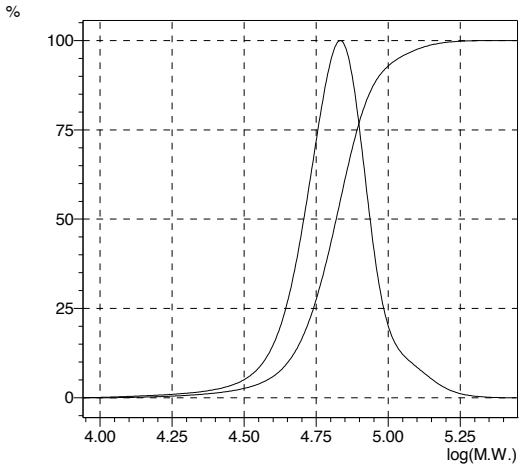
Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	12.958	12.958	281915	262
Top	14.168	14.168	68137	24421
End	15.925	15.925	8667	514

Area : 785040
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	61353
Weight Average Molecular Weight(Mw)	68659
Z Average Molecular Weight(Mz)	76017
Z+1 Average Molecular Weight(Mz1)	84869
Mw/Mn	1.11909
Mv/Mn	1.10356
Mz/Mw	1.10716

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	61353
Weight Average Molecular Weight(Mw)	68659
Z Average Molecular Weight(Mz)	76017
Z+1 Average Molecular Weight(Mz1)	84869
Mw/Mn	1.11909
Mv/Mn	1.10356
Mz/Mw	1.10716

Figure S6: SEC trace of isolated ε-PCL via ROP of ε-CL initiated by complex [**3a**][MeB(C_6F_5)$_3$]. Reaction conditions: ([**3b**][MeB(C_6F_5)$_3$]/BnOH/M_0) = 1/3/1500, neat ε-CL, 2h, 60 °C, 67% conv.

==== Shimadzu LCsolution GPC Analysis Report ====

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Sample ID	:
Vail#	:
Injection Volume	: 100 uL
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Batch Filename	:
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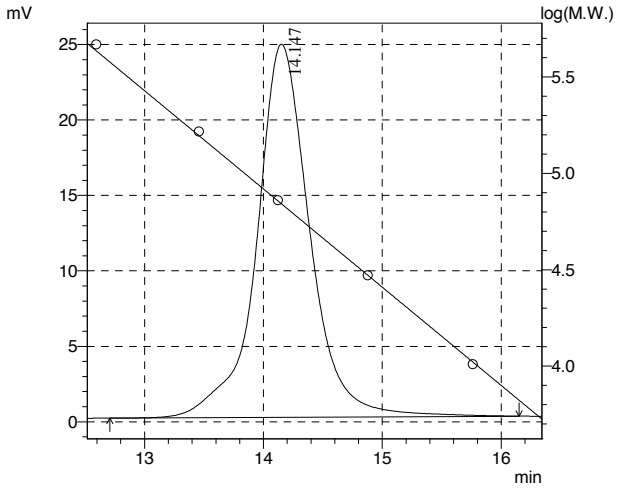
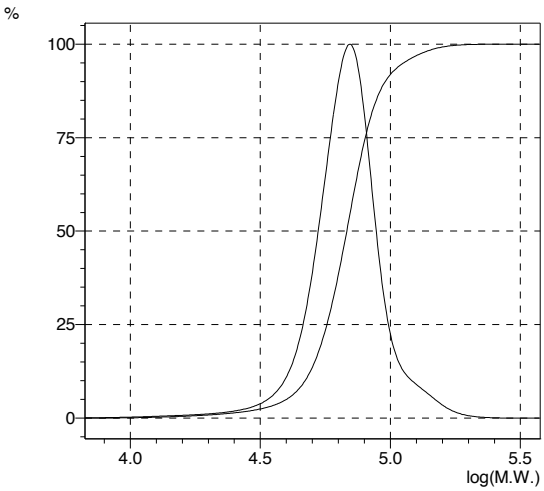
Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	12.708	12.708	378055	236
Top	14.147	14.147	69857	24745
End	16.150	16.150	6655	361

Area : 773718
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	62942
Weight Average Molecular Weight(Mw)	70932
Z Average Molecular Weight(Mz)	78721
Z+1 Average Molecular Weight(Mz1)	88449
Mw/Mn	1.12694
Mv/Mn	1.11100
Mz/Mw	1.10982

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	62942
Weight Average Molecular Weight(Mw)	70932
Z Average Molecular Weight(Mz)	78721
Z+1 Average Molecular Weight(Mz1)	88449
Mw/Mn	1.12694
Mv/Mn	1.11100
Mz/Mw	1.10982

Figure S7: SEC trace of isolated PCL via ROP of ε-CL initiated by complex [**3a**][$MeB(C_6F_5)_3$]. Reaction conditions : [**3a**][$MeB(C_6F_5)_3$]/BnOH/M_0 = 1/3/1000, THF, $[M]_0$ = 1M, 6h, 60 °C, 91 % conv.

X-ray crystallographic characterization of complex 4a.

A single crystal of complex **4a** was mounted on glass fibres and data collected on a Nonius Kappa-CCD or Bruker APEX II DUO Kappa-CCD area detector diffractometer (MoKα radiation, λ= 0.71073 Å). The complete conditions of data collection (Denzo software)[2] and structure refinements are in appendix section. All structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Table S1: Crystal data and structure refinement for complexes **4a**.

Compound reference	**4a**
Chemical formula	$C_{34}H_{38}N_2Zn$
Formula Mass	540.03
Crystal system	Monoclinic
a/Å	8.4247(4)
b/Å	19.9572(9)
c/Å	17.2470(8)
α/°	90.00
β/°	92.9430(10)
γ/°	90.00
Unit cell volume/Å^3	2896.0(2)
Temperature/K	173(2)
Space group	*P*21/*c*
No. of formula units per unit cell, Z	4
No. of reflections measured	25582
No. of independent reflections	8444
R_{int}	0.0321
Final R_1 values ($I > 2\sigma(I)$)	0.0464
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1201
Final R_1 values (all data)	0.0693
Final $wR(F^2)$ values (all data)	0.1337

[2] *Kappa CCD Operation Manual*, Nonius B. V., Ed.; Delft: The Netherlands, 1997.
[3] G.-M. Sheldrick, *SHELXL97, Program for the refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.